Studies on (η-Cyclo-octatetraene)(η^5-fluorenyl)titanium by Electron Spin Resonance and Electronic Absorption Spectroscopy

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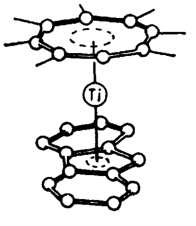
The compound (η-cyclo-octatetraene)(η^5-fluorenyl)titanium was studied by e.s.r. spectroscopy in fluid and frozen solutions and the e.s.r. parameters were accurately determined. The electronic absorption spectrum was also measured in the near-i.r. and u.v.–visible region. The correlation of these spectroscopic data with those of the previously studied η^5-cyclopentadienyl and η^5-indenyl analogues is coherent. The small variations are attributed to the electron-withdrawing effects of the benzo-substituents on the η^5-C_5 ring.

IN a previous paper[1] we reported a detailed e.s.r. and u.v.–visible study on the 17-electron titanium sandwich compounds [Ti(cot)L] [cot = η-cyclo-octatetraene; L = η-C_5H_5 (1), or η^5-C_9H_7 (2)] † and determined from the various spectroscopic parameters the extent of the unpaired-electron delocalization on each of the two η-bonded rings; we were able also to deduce a rough estimate of the magnitude of the charge borne by the metal.

In this work we report the results of an extension of this study to the isoelectronic compound [Ti(cot)L] (L = η^5-$C_{13}H_9$, fluorenyl ligand) (3). This compound was deemed worthy of special interest because of the fact that, apart from it being an additional member to this series of paramagnetic titanium metallocenes, it is one of the very few known transition-metal compounds with fluorenyl ligand forming part of a stable ferrocene-type structure.



(3)

EXPERIMENTAL

All manipulations were conducted under argon using rigorously dried solvents. The compound was prepared according to a procedure previously described in literature.[2] It was purified by sublimation under vacuum of the crude solid reaction product (after evaporation of the solvent) and freshly resublimed before use.

E.s.r. spectra were recorded on a JEOL ME 3X *X*-band spectrometer equipped with a BNM-12 Bruker n.m.r. gaussmeter for field calibration and a tunable resonant cavity for microwave-frequency measurements. Electronic absorption spectra were recorded in toluene solutions on a Cary 14 spectrometer.

RESULTS

The e.s.r. spectrum of (3) at room temperature in toluene solution exhibits features characteristic of a Ti^{3+} compound. It consists of a central set of lines due to superhyperfine interaction of the unpaired electron with the protons of the two η-bonded rings; satellites due to hyperfine interaction with ^{47}Ti and ^{49}Ti nuclei (I = 5/2 and 7/2, natural abundance 7.75% and 5.51% respectively) are clearly resolved at low field but substantially broadened at high field because of molecular tumbling. At −130 °C in toluene the spectrum is characteristic of a compound having an axial symmetry; hyperfine features due to the parallel components can be easily distinguished at high amplification with barely resolved superhyperfine splitting on both the parallel and perpendicular lines of the spectrum. In contrast to the frozen solution spectrum, the powder spectrum clearly shows three components of the *g* tensor due to the considerably narrower linewidth.

Both the frozen-solution and the powder spectra have been simulated using two computer programs. The first one calculates the theoretical e.s.r. spectrum by accumulating the spectra corresponding to a number of different orientations of the magnetic field towards the *g* tensor axes. The second operates a least-squares fitting of the theoretical spectrum against the experimental one. It incorporates the first program and allows calculation of a reliability factor R, $Y_{\text{calc.}}$ and $Y_{\text{obs.}}$ being respectively the calculated

$$R = 100\ (\Sigma_N|Y_{\text{calc.}} - Y_{\text{obs.}}|/\textstyle\sum_N|Y_{\text{obs.}}|)$$

and observed ordinates of the spectrum for each of the N steps of the magnetic field. The frozen-solution spectrum has been fitted to R = 12.5% using a slightly rhombic *g* tensor and a Gaussian lineshape with a linewidth of 13.3 G.‡ However, the best fit of the powder spectrum (R = 10.9%) is obtained for a Lorentzian lineshape and a linewidth of 3.7 G.[3]

For the toluene solution the principal components of the hyperfine tensor were determined from the liquid and frozen solution spectra by measuring $\langle A \rangle$ and $A_\perp$ assuming an axial symmetry. $A_\parallel$ was calculated from the relationship $\langle A \rangle = \frac{1}{3}(A_\parallel + 2A_\perp)$; $^{47,49}Ti$ satellites were not observed on the powder spectrum. The superhyperfine interaction is assumed to arise from delocalization of the unpaired electron on the η-C_8 ring (8 protons) and on the η^5-C_5 fluorenyl ring (1 proton). From computer simulation on the basis of

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† Systematic names for the η^5 ligands are 1—3a (7a)-η-indenyl [complex (2)] and 4(a,b),8a,9(9a)-η-fluorenyl [complex (3)].

‡ Throughout this paper: 1 G = 10^{-4} T.

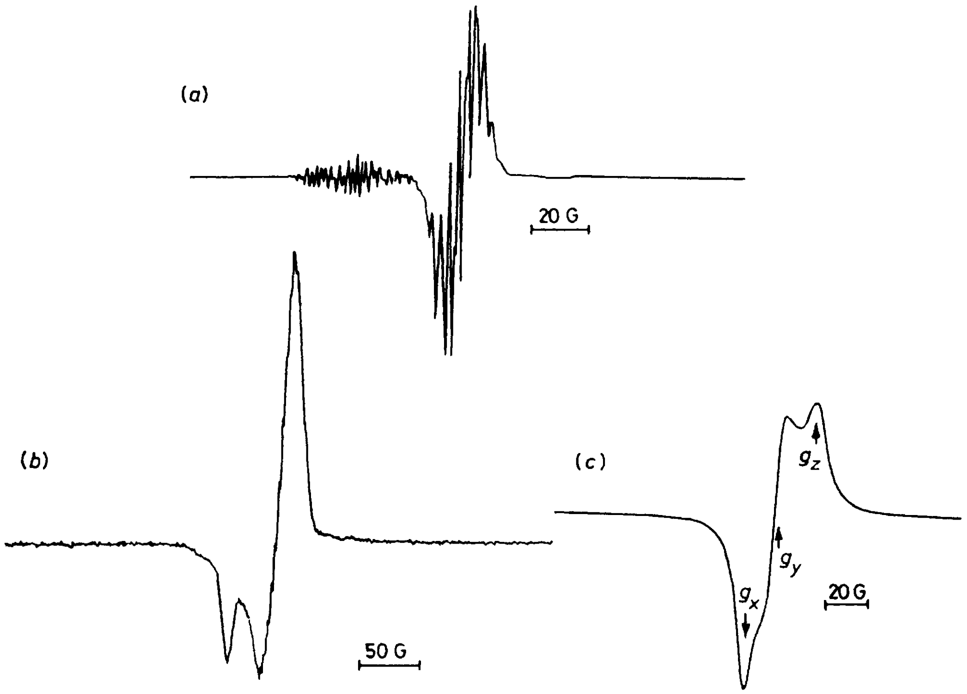

FIGURE 1 E.s.r. spectra of (3): (*a*) in toluene at 20 °C (the low-field signal is due to ^{47,49}Ti satellites); (*b*) frozen solution at -130 °C; (*c*) powder spectrum

parameters chosen roughly to match those determined for (1) and (2), the accurate values for a_H (fluorenyl) and a_H (cot) were determined.

The spectra relative to the three phases are shown in Figure 1 and the e.s.r. parameters are gathered in Table 1. Simulation of the spectra with different *g* values indicates that the *g* value uncertainty is about 0.001.

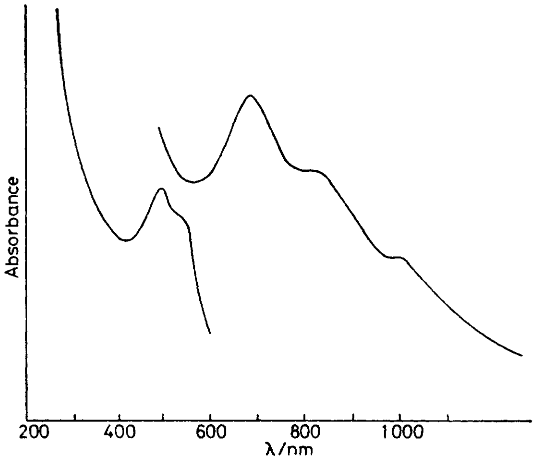

FIGURE 2 U.v.-visible and near-i.r. absorption spectrum of (3) in toluene

The u.v.-visible spectrum (Figure 2) shows absorption peaks at 19 800, 18 570, 14 390, 12 150, and 9 950 cm^{-1} (absorption coefficients could not be measured due to the extreme sensitivity of the compound to air and moisture).

DISCUSSION

Band assignments of the electronic absorption spectrum (Table 2) have been made according to the molecular orbital diagram proposed by Evans[1] for (1) and which we adapted to (2). The spectrum of (3) is strikingly similar to those of (1) and (2) so that the splitting of the e_1 (metal + cyclopentadienyl) degenerate level due to lowering of the symmetry of the indenyl compound (2) compared to (1) receives further confirmation with the fluorenyl compound (3) under study.

E.S.R. Spectra.—(*a*) *Fluid-solution spectrum.* In contrast to (1) and by analogy with (2), the e.s.r. spectrum of (3) is clearly resolved at room temperature both with regard to the hyperfine and superhyperfine structures; we relate this effect to the temperature-dependent rotation of the η^5-C_5 ring around the ring-to-metal bond axis, which is relatively fast for (1) and is considerably slowed down for (2) and especially (3) where the η^5-ring is heavily encumbered by the two benzo-substituents. This allows the sharp superhyperfine lines to be revealed

TABLE 1

Electron spin resonance parameters of compound (3) in fluid and frozen solutions[a]

	$\langle g\rangle$[b]	$\langle g\rangle$[c]	g_x	g_y	g_z	$\langle A\rangle$[b]	$A_\parallel$[c]	$A_\perp$	a_H (ligands)
Frozen solution (toluene)	1.979	1.980	1.966	1.975	2.000	14.8	4.2	20.1	1.87 (C_5 ring) 3.08 (C_8 ring)
Powder		1.980	1.984	1.981	1.975				

[a] Hyperfine constants in Gauss (G). *A* values relative to ^{47,49}Ti. [b] Measured in fluid solution. [c] Calculated values.

at room temperature for (2) and (3) whereas they are observable for (1) only at —40 °C.

(*b*) *Powder spectrum.* The powder spectrum of (3) exhibits g values rather different from those of the frozen solution. However, interestingly, the mean g value $\langle g \rangle = \frac{1}{3}(g_x + g_y + g_z)$ is identical with the g values measured for the frozen and liquid solutions. We believe that the different values for the powder arise from magnetic exchange interactions between near-neighbour metal centres. Indeed, the Lorentzian line-shape, and the much smaller linewidth compared to the frozen solution (3.7 G against 13.3 G), seems to indicate that the powder e.s.r. spectrum is exchange-narrowed;[4] without any information about the crystal structure of the compound we were unable to go further in the interpretation of the powder spectrum, and so we shall deal with the frozen solution where obviously such interactions are absent.

TABLE 2

Electronic absorption bands for compound (3)

Wavenumber/cm^{-1}	Transition
19 800 (sh)	$a_1 \leftarrow 2e_1$
18 570	
14 390	$a_1 \leftarrow e_2$
9 950	$3e_1 \leftarrow a_1$
12 150	

(*c*) *Frozen-solution spectrum.* The g_z value is very close to the free-electron g_e value. This is clear evidence that the unpaired electron resides in a d_{z^2} (a_1) orbital. Assuming a pure crystal-field model, one obtains the expressions for g_x, g_y, and g_z shown.[5,6] The small difference between g_z and g_e could arise from a small

$$g_x = g_e - \frac{6\lambda}{\Delta E(d_{z^2} - d_{yz})}$$

$$g_y = g_e - \frac{6\lambda}{\Delta E(d_{z^2} - d_{xz})}$$

$$g_z = g_e$$

contribution of $d_{x^2-y^2}$ in the ground state because of the rhombic (instead of the axial) symmetry of the complex. One could also think of a second-order contribution (in λ^2) to g_z,[7] but because of the small value of λ, this should be negligible. Substituting the ΔE values derived from the absorption spectrum in the above expressions for g_x and g_y, one obtains λ = 60.2 and 55.3 cm^{-1}. These values are quite similar to those found for compounds (1) and (2) (λ = 56.8 and 57.5 cm^{-1} respectively relative to $g_\perp$).

As for the A tensor, it was not possible to detect in the frozen-solution spectrum any resolution of the perpendicular hyperfine components into x and y components, so that an axial symmetry is assumed. In this case, the principal components of the A tensor in the crystal-field approximation can be calculated using the expressions shown below in which the first, second, and third terms stand respectively for the electron–nuclear isotropic and dipolar interaction and for the spin–orbit coupling correction. From the trend in band broadening at high field in the e.s.r. fluid-solution spectrum and taking into account the negative value of $P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$ and the expression of $A_\parallel$ and $A_\perp$, it can be shown that $A_\parallel$, $A_\perp$, and $\langle A \rangle = \frac{1}{3}(A_\parallel + 2A_\perp)$ are all positive. Taking $g_\perp = \frac{1}{2}(g_x + g_y) = 1.971$ one can deduce from the $A_\parallel$ and $A_\perp$ values: $P = -17.76$ G; $A_{\text{iso.}} = 14.43$ G. The accuracy of P and $A_{\text{iso.}}$ values resulting from the treatment of the A tensor with the assumption of an axial instead of rhombic symmetry is not substantially affected since the error would result from the third term of the above expressions which is a corrective one. Moreover, the difference between g_x and g_y is quite small. The λ and P values found indicate that the charge on the titanium ion in the compound is substantially reduced from the free-ion value. The formal charge on Ti in (3) is obtained from the plot of the calculated P values as a function of the charge on Ti ions in various oxidation states.[8] By interpolation for our experimental P value, one obtains a positive-charge value of 0.8 [as against 1 and 0.3 for (1) and (2) found in our earlier work]. Combining the results of the present study with those previously reported on (1) and (2) the following observations can be made.

$$A_\parallel = A_{\text{iso.}} + P[4/7 - 1/7(g_\perp - g_e)]$$

$$A_\perp = A_{\text{iso.}} + P[-2/7 + 15/14(g_\perp - g_e)]$$

(*a*) In all the three compounds, the formal positive charge on Ti is substantially lower than three. Such an effect, which is usually observed when charged ligands interact with a metal ion, has been discussed by McGarvey[8] and others. However, the e.s.r. spectrum clearly originates from a d^1 ion, so that the charge reduction should be viewed as a screening effect of the ligands rather than a true charge transfer to the metal ion.

(*b*) The proton hyperfine coupling is higher for the C_8 ring than for the C_5 ring. This has been related in an earlier ENDOR study to the closer distance of the C_5 ring protons to the nodal cone of the Ti d_{z^2} orbital.[9] Similar observations were also made on some chromium mixed sandwich compounds.[10]

(*c*) The proton hyperfine coupling constants follow a monotonous trend, with a_H(cot) decreasing (3.24, 3.15, 3.08 G) and a_H (η^5-C_5) increasing (1.62, 1.64, 1.87 G) along the series (1), (2), and (3) respectively. Thus it appears that loss of electron density on the cot ring is related to the effect of the electron-withdrawing substituent on the C_5 ring which is more pronounced in (3) than in (2), when compared to (1).

A more precise evaluation of this effect deduced from measurements of oxidation potentials will be reported later.

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